BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

THE LEAD-URANIUM-THORIUM RATIO OF SPRUCE PINE,
NORTH CAROLINA, URANINITE

by

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(B.Ch.E., Northeastern University, 1932)

Submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

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ACKNOWLEDGMENT

To Doctor Chester M. Alter, I really owe the
success of this problem. His constant, untiring ef-
forts in my behalf were an inspiration which I never
shall forget.

I gratefully acknowledge the kindly interest
shown by Doctor Edward O. Holmes, Jr., and Doctor
John Phillip Mason.

INDEXED OUTLINE

INTRODUCTION

The first scientific problem which claimed the attention of scientists was: "How old is this earth of ours?" The records of ancient philosophers are not consistent on this point. Man, in addition to taking delight in forecasting and predicting the physical future of the world, has always yearned to know, as certainly as possible, the actual a ge of the earth.

The purpose of this research is to supplement available data and chemical procedure relative to the determination of the age of the earth by means of radio-activity.

The results of this investigation will either emphasize the accuracy of present existent methods, or at least indicate the weak points present in the general procedures used in the determination of the lead-uranium-thorium ratios in radio-active minerals.

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HISTORICAL

Various methods have been advanced by which the age of the earth has been determined. The most important of these methods are very obviously based on physical evidence. There are many methods of measuring geologic time suggested by recent developments in physics, to the data of which additions have been rapid. Among these are: the relative proportions of oxygen isotopes, or deuterium (heavy hydrogen), in waters or minerals; and astronomical considerations as to an expanding universe. However promising for the future these methods may be, they have not, at present, arrived at a stage of geological value to compare with the following principal methods:

(a) Geochronology, or the age of the earth on the basis of sediments and life.

(b) Age of the earth from the age of the ocean, which is estimated by dividing the total sodium content of the ocean, by the amount poured yearly into it by the rivers of the world. The assumptions that underlie this procedure are: (1) there was no sodium in the primeval ocean; (2) the sodium washed into the ocean has been steadily accumulating, the amount lost by precipitation being negligible; and (3) the annual increment determined from present-day data has been consistent throughout geologic time.

(c) Calculation of the age of minerals from radio-activity data

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(c) Calculation of the age of minerals from radio-activity data

and principles.

(d) The age of the earth based on astronomical data.

The oldest method we know for determining the length of geologic time is based on the thickness of the strata that accumulated during that time. Quite often estimates of this kind have been advanced, but as our knowledge of the earth increases, the known thickness of the strata has steadily increased. It is believed that eventually the pile of strata for the world will total approximately 400,000 feet. To convert this thickness accurately into years, is still an unsolved problem.

Those methods of age-determination based on radio-active disintegration involve the least number of assumptions. The basis for these methods is the fact that the radio-active elements uranium and thorium disintegrate spontaneously at constant determinable rates and yield a stable product--lead--whose atomic weight varies according to the proportion contributed by the radio-active parents.[1] The disintegration of uranium and thorium proceeds according to the laws of a monomolecular reaction, as first pointed out by Rutherford, and if the disintegration constant is accurately known, the age of a uranium-bearing mineral can be readily and accurately determined by means of Kovarik's formula.[2]

In building up a geologic time-scale in years based on atomic disintegration, the following conditions should be observed:

(1) The minerals must be unaltered; i.e., not changed by leaching by surface waters, or by other external processes since it was originally formed..

[1] Bulletin 80, National Research Council, p. 4 (1931).

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(2) The contents of U, Th, and Pb must be determined. Preferably these elements should be present in considerable amounts, so that the analytical errors will be minimized.

(3) The atomic weight of lead should be determined, on lead obtained from material analyzed for U, Th, and Pb.

(4) The geologic age of the mineral should be known.[1] These requisites must be rigorously fulfilled, and many currently accepted age-determinations rest on shaky foundations due to failure in following at least one of these items. In the future, it is probable that two more conditions must be met: (1) the material should be radiographed, in order to determine its homogeneity; and (2) the ratio of actinium to uranium should be determined.

The pioneer in this field of age-determination by means of radio-activity and principles is B. B. Boltwood.[2] He originated the method of determining the age of minerals from the amounts of uranium and lead present in a primary mineral. Boltwood was among the very first who contributed experimentally to the proof of the disintegration theory of radio-active elements propounded by Rutherford and Soddy in 1903.[3] Believing firmly in the disintegration theory and observing that lead is present in all radio-active minerals, Boltwood came to the conclusion that the lead in these minerals was the final disintegration product of uranium, thorium, and actinium according to the type of mineral. He found, however, that the amount of lead per gram of uranium varied considerably from mineral to mineral. He, therefore, arranged the minerals according to their lead-uranium ratio, and drew attention to the fact

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that the increasing ratio corresponded to the increasing age of the geo-
logical formation in which the minerals were found.

The presence of various isotopes of lead, uranium, and thorium
necessitated ordinarily the making of corrections for these variables.
However, since these variables lie outside the scope of this investiga-
tion, they will not be considered. In applying the disintegration theory
to age-determinations, the assumption must be made that at the time the
mineral was formed, uranium, thorium, and lead may have been present in
any amounts. Since that time, then, these elements have been disinte-
grating according to the law of radio-active disintegration, resulting
in a cumulative deposit of radiogenic lead.

By means of radio-active disintegration, uranium of atomic weight
238.14, will yield as an end-product, radiogenic lead of atomic weight
206 or 207, depending upon whether it has been generated by the radium
series or the actinium series. When thorium of atomic weight 232.12,
disintegrates, the end-product is a radiogenic lead of atomic weight
208.

Both uranium and thorium undergo this process of radio-active dis-
integration by means of a constant emission of alpha and beta particles.
The beta particles having zero mass, do not affect the mass of the end-
product. The alpha particles, however, possess a mass of four; there-
fore, each time an alpha particles is emitted, the resulting element
is lower in atomic weight by four units. It would be interesting to
follow the path of this radio-active disintegration in the case of ura-
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Uranium emits eight alpha particles in disintegrating. This can

be verified by the amount of helium produced, since a helium atom is merely an alpha particle which has acquired two electrons. The loss, therefore, of eight alpha particles results in a net loss of thirty-two units in atomic weight:

U	Pb	8 He
238	206	32
239	207	

It has been observed that thorium emits a total of six alpha particles in the course of its disintegration, and therefore there is a loss of approximately twenty-four in atomic weight.

Th	Pb	6 He
232	208	24

From the rates of production of helium from uranium and thorium, the rates of production of lead from both these elements have been calculated.

The two most common radio-active disintegration methods for the determination of the age of the earth are (1) the helium method and (2) the lead method. Of these two methods, the latter by far is the most important and the one most commonly used.

Rutherford was the first to draw attention to the possibility of determining the age of a radio-active mineral from the knowledge of its helium and uranium contents. We know, to-day, that the alpha particle is the nucleus of a helium atom and we do not know (by experiment) of any other source of helium. Consequently, if the accumulated alpha particles within a mineral do not escape from the mineral, we could calculate the age of the mineral from analysis data given the amounts of the helium, uranium, and thorium, assuming knowledge of the radio-active series and the disintegration constants. However, there is a leakage of

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helium from a radio-active mineral, at least under laboratory conditions. For this reason, the amount of helium found by analysis must be too small to account for the alpha particles emitted during the age of the mineral and consequently the value for the age so obtained can only represent the lower limit of the age of the mineral. Figures show an enormous discrepancy in the value obtained by the helium method and that obtained by the lead method.

For obtaining the age formula in the lead method, the following method of reasoning is used:

Let $1/C$ represent the amount of lead produced by one gram of uranium in one million years. Then, the lead-uranium ratio of any crystal, divided by the constant $1/C$ would represent the approximate age of the mineral; or written in equation form:

Approximate Age $= Pb/U \times C$ million years,

where Pb, and U represent respectively the percentage of lead and uranium in the mineral.

Thorium also generates lead which accumulates with that produced by the uranium. This must also be taken into consideration. For a pure thorium mineral we have an identical equation:

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Since in most uraninites, both uranium and thorium occur, it is necessary to convert their respective contents to a uniform basis of equivalent lead-producing power. This is done by multiplying the thorium content by a constant "K" which is the amount of uranium equivalent to one gram of thorium in lead-producing power. The equation for the approximate age is:

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$$\text{Approximate Age} = \frac{Pb}{U + 0.36 \, Th} \times 7600 \text{ million years}$$

This formula is often referred to as "Kovarik's formula".[1]

There are a great number and variety of radio-active minerals containing variable amounts of lead, uranium, and thorium. Although the percentages of these elements vary from mineral to mineral, the lead-uranium ratio is fairly constant within minerals of approximately the same geological age.

A number of independent investigators are of the opinion that uraninite is one of the best minerals with which to work. The advantage of uraninite over other minerals is its relative purity and regular crystal form. The lead, uranium, and thorium contents are relatively high, thus making an accurate analysis somewhat easier.

There are various sources of uraninite, among which are those from Keystone, South Dakota; Smyaga Pala, Carelia, Russia; Flat Rock mine, North Carolina; Katanga mines in the Belgian Congo; and those from the Wilberforce regions in Ontario, Canada.

Uraninite is a general term for crystalline uranium oxide. It occurs as crystals or large crystal masses, embedded in feldspar, or as crystals attached to the feldspar margin intersown with magnetite. The lea st altered or freshest uraninite is that which is wholly embedded in surrounding minerals. The crystals are well-formed, and predominantly cubic. It has a specific gravity between 9.0 - 9.7 The fracture is conchoidal to uneven and it has a lustre ranging from submetallic to greasy. Uraninite is velvet-black, commonly with a grayish, greenish,

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[1] Bulletin 80, National Research Council, p. 75 (1931).

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The crystal of uraninite used in this research was probably originally obtained from Flat Rock mine, Spruce Pine, Mitchell County, North Carolina, and then was obtained by us from the Smithsonian Institute. The uraninites from this region are generally referred to as "Spruce Pine" uraninites or pitchblendes.

Among the most recent work done on uraninite is that on Wilberforce uraninite by Todd and Ellsworth. Todd[1] has found the lead-uranium ratio to be 0.150, which corresponds to an age of 1140 million years. Ellsworth[2] has analyzed two uraninites, one altered and the other fresh or unaltered. The fresh uraninite had a ratio of 0.157, corresponding to an age of 1193.2 million years which is in fair agreement with that obtained by Todd. The altered uraninite, however, had a lead-uranium ratio of 0.171, corresponding to an age of 1299.6 million years. Alter and Kipp,[3] reverting to division of the single crystal into three layers by means of acid, obtained a lead-uranium ratio of 0.2175, which corresponds to 1653 million years. Alter and Yuill[4] divided a single crystal of Wilberforce uraninite mechanically into three sections and obtained a lead-uranium ratio of 0.1736, corresponding to 1319.3 million years.

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[1] Bulletin 80, The National Research Council, p. 328 (1931).

[2] Ellsworth: Am. J. Sci., (5) 9, 127 (1925) and Am. Mineral., 15, 455 (1930).

[3] Alter and Kipp: Ibid., 32, 120-128 (1936).

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METHOD AND PROBABLE VALUE OF ANALYSIS

Work done by previous investigators has been based on the general assumption that the minerals have altered to a very slight degree, if at all, and that the lead, uranium, and thorium have all been leached out at the same rate.

The value of the lead-uranium ratio would be quite trustworthy, if we could be assured of the fact that none of the radio-active elements of our mineral had been leached out by outside agents of nature. Again, our results would be satisfactory if we were sure that the radio-active elements present have been leached out in the same proportion as they existed in the mineral. However, the consensus of qualified opinion has it that alteration does take place and that the elements of nature preferentially leach out the various radio-active elements present at variable rates.

Ellsworth[1] claims that "it is evident from present theories that the alteration of radio-a ctive minerals is due to two causes. Firstly, internal alteration due to auto-oxidation, secondly, alterations involving oxidation, hydration, and silication due to purely external natural agencies. The first is probably the initiating cause of the second since by auto-oxidation volume increase probably occurs which results in shattering not only the mineral itself but the surrounding rock, thus

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Bulletin 80, The National Research Council, p. 298 (1931).

increasing permeability to solutions and gases."

Alter and Kipp[1] have shown that the effects of leaching, if any, only penetrate to a certain depth and therefore, by utilizing only the innermost core of the crystal, the leaching effects would be absent, and the data, therefore, more trustworthy as far as its bearing on the age of the crystal is concerned.

It has been pointed out[2] that certain crystals of uraninite appear altered and Ellsworth[3] has explained the reason for this rather satisfactorily. The majority of investigators admit the possibility of preferential leaching and many of them recently have cleansed the crystal of a thin section of outer coating assuming that most of the apparently altered portion of the crystal will be removed thereby. However, this is not an assurance that all of the actually altered portion has been removed, for the actual extent of the leaching effect has not been determined in many of the cases. It was merely assumed that the above precaution would be sufficient.

Ellsworth, when analyzing an altered uraninite obtained a lead-uranium ratio of 0.171 which was considerably higher than the results obtained for the fresh uraninite (0.157). The relatively high value of Ellsworth's altered uraninite would seem to indicate several possibilities. Ellsworth has concluded that weathered specimens of uraninite tend to give higher ratios than fresh ones of the same age. He states[4]

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[4] Ibid., p. 328.

that "this may not always be the case, but it appears to be theoretically reasonable inasmuch as lead compounds formed by weathering are probably on the whole less soluble than similar uranium compounds. This, however, is a point which requires much more investigation." There is a probability that both lead and uranium have been leached out more or less preferentially.

The lead ratios of Carolina uraninites, unlike Wilberforce specimens, vary widely but in keeping with this variability, there is evidence of the presence of original lead in the minerals, since the atomic weight of lead separated from North Carolina uraninites was found by Richards and Lambert to be 206.40.[1] Unfortunately the analysis by Hillebrand[2] in 1891 and the atomic weight determination by Richards and Lambert in 1914 were not made on the same material. However, using these results and applying Kovarik's formula, an age of 251 million years was obtained and a lead-uranium ratio of 0.034. Although thus fraught with much doubt, these determinations are the best we have on the age of these uraninites.

It is the object of this investigation to analyze a single crystal of North Carolina uraninite in the light of present theory and attempt to eliminate certain points of doubt. The author intends to save the Pb obtained from this crystal in order that another investigator may determine its atomic weight. The use of this figure in our calculations will make them more accurate. The crystal was mechanically divided into three sections and analyzed separately, since Alter and

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Kipp, and Alter and Yuill, among others, have shown that erroneous re-sults may be obtained in age-determination, if even a single crystal in its entirety is ground and analyzed. It is important that further quantitative data be brought to bear on the subject and therefore the author has analyzed, by special method of analysis, a single crystal of Spruce Pine, North Carolina Uraninite.

W. F. Hillebrand[1] using a uraninite from Flat Rock mine, Spruce Pine, Mitchell County, North Carolina, got a lead-uranium ratio of 0.050 and 0.053, whereas Boltwood,[2] a few years later, obtained a lead-uranium ratio of 0.049. This result is in almost perfect agreement with that of Hillebrand.

Another object, therefore, of this investigation, was to determine as far as possible whether mechanical division of the crystal into layers, and new methods of procedure will affect the lead-uranium ratios, and also to discover how the author's results will compare with these earlier ones.

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EXPERIMENTAL PROCEDURE
PREPARATION OF SAMPLES

The crystal was a rather well-developed one, a part of a collection of material from the North Carolina locality, weighing approximately 38 grams and obtained from the Smithsonian Institute. The specimen carried very little of the usual surface alterations products and exhibited very distinct crystal faces and angles.

The single crystal of uraninite as received was first thoroughly cleansed by vigorous scrubbing and rinsing with water. After drying at 105 degrees C., it was carefully weighed. It was then divided into three parts, outer, middle, and core, by carefully removing successive parts by means of a steel file. Each face was filed down an equal amount, great effort being taken to maintain the original form of the crystal during the process of filing off the outer portions. The outside, middle, and core portions weighed 15.1 g., 12.8 g., and 9.4 g., respectively.

The particles of steel introduced in the samples were removed by very thorough magnetic separation.

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ANALYSIS FOR LEAD, URANIUM, AND THORIUM
GENERAL PRINCIPLE

In general, the method reported by Doctor John Putnam Marble in
a private communication, was used in the determination of lead and ura-
nium. The thorium was precipitated as thorium sebacate. Because this
particular specimen was a remarkably pure uraninite, certain precau-
tions often necessary were found to be without value. The lead was
first precipitated as the sulfide and then as sulfate, in which form
it was weighed. Thorium and uranium were twice precipitated as hydrox-
ide. After dissolving the combined hydroxides in nitric acid, the
thorium was precipitated as oxalate, dissolved, and reprecipitated
with sebacic acid. Thorium sebacate was ignited to ThO_2 and then was
weighed. The uranium was precipitated as ammonium uranate, ignited
and weighed as U_3O_8.

ANALYTICAL PROCEDURE
DETERMINATION OF LEAD

Grind the sample thoroughly and weigh out samples by difference.
The samples for a complete analysis should weigh about 0.65 to 0.75
grams. Cover the samples with a little distilled water, and add about
50 ml. of 1:1 redistilled nitric acid. Acid concentration much larger
than this will prevent the complete precipitation of lead as sulfide,
and less than this will not prevent the precipitation of uranium as
sulfide. After the first vigorous evolution of helium has stopped,
heat the flasks gently so that the gas just continues to be evolved.
This heating may be done by the use of small gas flames. However, it
was found that it was more convenient to use hot plates since the tem-
perature could be more easily controlled over a long period of time.
The heating is continued until no more helium is evolved, or for about
six hours. By this time, the residue of silica should be practically
white in color. During the heating, the flasks should be kept covered
in order to prevent the loss of too much of the nitric acid.

The solutions are now diluted to 200 ml. and allowed to cool. The
silica is then filtered off and the filtrate is saved for the rest of
the analysis. The silica is thoroughly washed, and then may be ignited
and weighed.

The filtrates are now evaporated to dryness in order to get rid
of as much of the nitric acid as possible. They are then dissolved in
a little water and any excess acid is neutralized with a little re-

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The filtrates are now evaporated to dryness in order to get rid of as much of the nitric acid as possible. They are then dissolved in a little water and any excess acid is neutralized with a little re-

distilled ammonium hydroxide. When the solutions are neutral, 5 ml.
of redistilled nitric acid are added and the solutions are diluted to
400 ml. It was found that if the flasks were now washed down with a
very dilute solution of ammonium hydroxide it prevented the precipita-
tion of so much sulfur when the hydrogen sulfide is passed in. Pass
in washed hydrogen sulfide for two or three hours while the solutions
are cold and then heat them to boiling for about fifteen minutes with
the hydrogen sulfide still passing in. This procedure will help coagu-
late the precipitate. Allow to cool slowly, filter, and wash thorough-
ly.

Test the filtrate for complete precipitation by again passing in
washed hydrogen sulfide for about an hour and again heating to boiling
for about fifteen minutes. Cool slowly and filter as before.

The lead sulfide is washed as thoroughly as possible into an
evaporating dish. The filter paper is ignited at a low temperature,
and the residue dissolved in nitric acid. The flask in which the pre-
cipitation was carried out is washed thoroughly with nitric acid, and
all three of these are put together. The whole is digested for several
hours with concentrated nitric acid, and is then baked out almost to
dryness. The residue is then dissolved in water and the sulfur is
filtered off and ignited. The residue after the ignition of the sulfur
is dissolved in nitric acid, filtered, and added to the rest. Evapo-
rate to dryness, add 2 or 3 ml. of nitric acid to keep other salts in
solution and dissolve in 50 ml. of water. Add excess dilute sulfuric
acid and evaporate to fumes of SO_3. Add 40 ml. water and allow to
stand overnight. Transfer the solution and precipitate to weighed

platinum crucibles. Fume off the sulfuric acid and heat the lead sul-
fate to constant weight using a radiator arrangement.

SEPARATION OF THORIUM AND URANIUM

The filtrate from the lead precipitation is then made to almost
600 ml., either by diluting it or by evaporation. It is then boiled to
drive off the hydrogen sulfide. About 15 ml. of 1:1 redistilled nitric
acid are then added, and the solution is again boiled to drive off
carbon dioxide. Excess ammonium hydroxide is then added and the solu-
tion is kept near boiling while the precipitate is allowed to settle.
The solutions are then filtered while still hot. Wash with hot, very
dilute ammonium hydroxide. Dissolve the precipitate in as little di-
lute nitric acid as possible, dilute to about 600 ml. and boil. Again
add excess freshly distilled ammonium hydroxide, allow to settle, and
filter hot. Any uranium is then recovered from the combined filtrates
by evaporating to dryness several times with excess nitric acid or
aqua regia.

It was found that if this evaporation were carried out on a water
bath, it was a very lengthy affair. Also, if it were carried out in
ordinary evaporating dishes which hold about 200 ml., there was a danger
of loss by spattering when the excess acid was added. The fastest and
safest way to carry out this procedure seemed to be to evaporate the
solutions in large beakers on the hot plates. In this way they could
be kept just below boiling, and if any spattering occurred when the
solutions dried, the beakers were large enough to prevent any loss.

After the ammonium salts have been driven off by this repeated

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evaporation with excess acid, the residue is dissolved in a little con-
centrated nitric acid and any uranium or thorium is precipitated as be-
fore. All the uranium and thorium precipitated by the ammonium hydrox-
ide is then dissolved in nitric acid. The resulting solution is then
evaporated to dryness. Add 4 ml. of redistilled nitric acid and a
little water. This should dissolve the residue. Now dilute to 320 ml.
and pour this solution into 80 ml. of 10% oxalic acid solution. Either
allow this to stand three or four days or digest for 24 hours in a
water bath. Allow to cool thoroughly and filter. The thorium is pre-
cipitated as thorium oxalate, and the uranium remains in the filtrate.
The precipitate should show no traces of yellow; it should be pure white.

DETERMINATION OF THORIUM

There are two ways of treating the thorium oxalate precipitate.
The filter paper and precipitate may be transferred to a platinum cru-
cible and the carbon charred and burned off. The residue is then
roasted to constant weight with a meker burner. The oxides so obtained
are then fumed to dryness with 10 ml. portions of redistilled sulfuric
acid until they are pure white in color. This process is very slow
and has to be repeated several times so that the whole may take weeks.
When the residue is pure white, it is soluble in nitric acid, and is
so dissolved, and it may be necessary to digest it with concentrated
nitric acid for several hours before it will all be in solution.

The other way of treating the oxalate precipitate is to dissolve
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Whether the procedure has been carried out in the first or the
second way, the nitric acid is neutralized with fresh ammonium hydrox-
ide. If there was a large amount of acid used to dissolve the precipi-
tate, it is better to evaporate most of it off before neutralizing with
the ammonium hydroxide. Make the solution up to about 100 ml. and heat
to boiling. Add solid recrystallized sebacic acid to excess. As it is
added, the thorium sebacate will precipitate first as a rather crystal-
line white precipitate, but as more sebacic acid is added, it will not
dissolve and can be distinguished from the thorium sebacate in that it
is much more flacculent. The sebacic acid should be added until a
little of this undissolved sebacic acid is evident. Filter the solu-
tion while it is still very hot. Wash the precipitate free of sebacic
acid with hot water, and dissolve it in dilute nitric acid. Neutralize
the acid and reprecipitate as before. Reprecipitate until the precipi-
tate is pure white in color. Burn off the filter paper in weighed
platinum crucibles and ignite the precipitate to ThO_2. This requires
about four hours of heating with a meker burner. Heat the precipitates
to constant weight.

Determination of Uranium

Concentrate the filtrate from the separation of thorium and urani-
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When all the oxalic acid is gone, dilute with water to several hundred mls. Prepare some ammonium hydroxide solution by taking about 150 ml. of freshly distilled and saturating it with ammonium carbonate. Add this solution to the uranium solution until methyl red just turns yellow. Then add about 2 ml. excess. It is sometimes necessary to add a little solid ammonium carbonate at this point to prevent the precipitation of uranium. Heat the solutions gently until carbon dioxide begins to be evolved. Remove from flame and allow the precipitates of iron and aluminum hydroxides to settle. Filter, and wash thoroughly with dilute ammonium carbonate solution and finally with hot dilute ammonium nitrate solution until the precipitate no longer smells of ammonia.

Very carefully add nitric acid to the filtrate until the red color of the methyl red returns. It is very necessary to keep the beaker covered with a watch glass while this acid is being added since carbon dioxide is given off very vigorously and will cause loss by spattering

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unless the beaker is carefully covered. Wash down the cover glass and then evaporate to dryness several times with excess acid to get rid of the ammonium salts. Dilute to several hundred mls. and precipitate any iron or aluminum as before. Then again carefully neutralize the filtrate and rid it of ammonium salts.

The precipitate iron and aluminum hydroxides should be dissolved in dilute nitric acid and reprecipitated. The filtrate from the reprecipitation is added to the main filtrate containing the uranium. Ammonium salts are removed from these combined filtrates as before.

Dilute the filtrate to about 500 ml. and boil to remove any carbon dioxide. Add excess of freshly prepared ammonium hydroxide, allow to settle, and filter hot. The solution is kept near the boiling point during filtration to prevent the absorption of carbon dioxide which would render the uranium soluble as ammonium uranyl carbonate. Remove traces of uranium from the filtrate as before. Dissolve the precipitates in dilute nitric acid and reprecipitate.

Place the precipitates in weighed platinum crucibles and place these in a slanting position with the covers slanting. Burn off the filter paper carefully. Place the crucible in an upright position and blast with a full meker flame. There should be no trace of yellow after the precipitates have been blasted long enough. Heat the U_3O_8 to constant weight.

The sebacic acid method for thorium,[1] according to Dr. J. P. Marble,[2] may give results that are a trifle high while the peroxynitrate method, more generally used, may give slightly too low results.

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In the method of analysis outlined above, provision was made for the separation of iron and aluminum from uranium. In the two inner sections, these elements were absent and only a trace was found in the outside section. The removal of this trace will make our value for uranium in the outside section more trustworthy.

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A TYPICAL CALCULATION

In determining the percentage composition of an element or compound, the following method is usually followed:

Weight of Sample

Weight of Core Sample 0.41000

Weight of Element (thorium)

Final constant weight of ThO_2 . . . . 0.00630

Corresponding weight of Th. 0.00554

Weight of Element (ThO_2 X conversion factor). 0.00554

Percentage of Element in Sample

Weight of Thorium 0.00554

Weight of Sample. 0.41000

Quotient of Thorium by Sample 0.01350

Percentage of Element Thorium . . . . 1.350 %

In like manner the percentage compositions of lead and uranium in each section are computed.

Computation of the Age from Composition Data

Average percentage composition of lead . . . . 2.316 %

Average percentage composition of uranium . . . . 51.311 %

Average percentage composition of thorium . . . . 1.318 %

$$\text{Lead-uranium ratio} = \frac{Pb}{U \pm 0.36\ Th} = \frac{2.316}{51.311 \pm 0.36\ (1.318)} = 0.04472$$

In determining the percentage composition of an element or compound, the following method is usually followed:

Weight of Sample

Weight of Core Sample 0.41000

Weight of Element (thorium)

Final constant weight of ThO₂ 0.00850

Corresponding weight of Th 0.0054

Weight of Element (ThO₂ X conversion factor). . . 0.0054

Percentage of Element in Sample

Weight of Thorium 0.0054

Weight of Sample. 0.41000

Quotient of Thorium by Sample 0.01350

Percentage of Element Thorium . . . . 1.350 %

In like manner the percentage compositions of lead and uranium in each section are computed.

Computation of the Age from Composition Data

Average percentage composition of lead . . . . . . 2.316 %

Average percentage composition of uranium . . . . 91.311 %

Average percentage composition of thorium . . . . 1.318 %

$$\text{Lead-uranium ratio} = \frac{Pb}{U + 0.36 \ Th} = \frac{2.316}{91.311 + 0.36 \ (1.318)} = 0.04472$$

The approximate age of this section is the product of this ratio
by the constant 7600 million years or 0.04472 x 7600 = 339.872 million
years.

The following is a table of the percentages of lead, uranium, and
thorium in each of the three sections of the crystal and of the crystal
as a whole.

TABLE

Section of crystal	Analysis	Lead	Lead Lost	Uranium	Thorium	Pb/U+Th
Octahia	1					
	2					
	3					
	Av.	1.905			0.756	0.04468
Middle	1					
	2					
	3					
	Av.				0.591	0.04047
Base	1				1.408	
	2	0.561			1.260	
	3	0.475			1.366	
	Av.	0.540			1.318	
Weighted average for whole crystal					1.096	0.04138

The approximate age of this section is the product of this ratio by the constant 7600 million years or 0.04472 x 7600 = 339.872 million years.

EXPERIMENTAL RESULTS

The following is a table of the percentages of lead, uranium, and thorium in each of the three sections of the crystal and of the crystal as a whole.

TABLE I

Section of crystal	Analysis	% Insoluble	% Lead	% Uranium	% Thorium	$\dfrac{Pb}{U + 0.36Th}$
Outside	1	2.342	1.836	59.587	0.739	
	2	1. 892	1.842	_____	0.749	
	3	1.744	_____	59.897	0.719	
	Av.	1.993	1.839	59.742	0.736	0.03065
Middle	1	1.783	2.640	62.533	_____	
	2	1.499	2.500	63.168	1.353	
	3	1.772	2.557	63.067	1.329	
	Av.	1.685	2.566	62.923	1.341	0.04047
Core	1	0.485	2.328	51.911	1.350	
	2	0.361	2.304	50.937	1.240	
	3	0.473	_____	51.085	1.364	
	Av.	0.440	2.316	51.311	1.318	0.04472
Weighted Average for Whole Crystal			2.209	58.709	1.090	0.03738

The following is a table of the percentages of lead, uranium, and thorium in each of the three sections of the crystal and of the crystal as a whole.

TABLE I

Section of crystal	Analysis	% Insoluble Lead	% Lead	% Uranium	% Thorium	$\frac{Pb}{U + 0.36Th}$
Outside	1	2.543	1.856	59.587	0.759	
	2	1.892	1.847	_____	0.740	
	3	1.744	_____	59.897	0.719	
	Av.	1.993	1.859	59.742	0.756	0.03065
Middle	1	1.783	2.640	62.533	_____	
	2	1.499	2.500	63.168	1.353	
	3	1.772	2.557	63.087	1.329	
	Av.	1.685	2.566	62.923	1.341	0.04047
Core	1	0.485	2.528	51.911	1.350	
	2	0.351	2.304	50.597	1.240	
	3	0.473	_____	51.085	1.364	
	Av.	0.440	2.316	51.311	1.318	0.04472
Weighted Average for Whole Crystal			2.209	58.709	1.090	0.03736

The following includes a table of the lead, uranium, thorium ratios of each section of the crystal, and of the entire crystal.

TABLE II

Ratio of the Outside Section 0.03065

Ratio of the Middle Section 0.04047

Ratio of the Core Section 0.04472

Ratio of the Entire Crystal 0.03738

TABLE III

Resultant Age Value for the Outside Section:-

232.940 million years.

Resultant Age Value for the Middle Section:-

307.572 million years.

Resultant Age Value for the Core Section:-

339.872 million years.

Resultant Age Value for the Entire Crystal:-

284.088 million years.

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CONCLUSIONS

1. According to Ellsworth, a very low silica content indicates
that the mineral has not suffered appreciable leaching, alteration,
or replacement by circulatory waters. Thus, as Ellsworth remarks,[1]
"if this theory is correct, we have a method for judging the probable
value of age results. If the mineral contains little or no silica we
may attach considerable weight to the age result; if an appreciable
amount of silica is present we can be almost certain that the age re-
sult is lower--often very much lower--than the true value." Available
data, together with the results of this investigation, clearly sup-
port this theory with remarkable consistency. As the amount of in-
soluble matter increased, the lead-uranium-thorium ratio correspending-
ly decreased resulting in a lower age result.

2. The lead-uranium-thorium ratiosof the two inner sections are
rather close and yet vary considerably from the lower ratio of the out-
side section. This suggests that:

    (a) the crystal has been affected appreciably by altera-
        tion;

    (b) the leaching effect has penetrated the outside sec-
        tion and possibly the outer fringe of the middle
        section causing the slight variation in ratio from
        that of the core which has not been affected by

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[1] Bulletin 80, The National Research Council, 328 (1931).

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CONCLUSIONS

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2. The lead-uranium-thorium ratios of the two inner sections are rather close and yet vary considerably from the lower ratio of the outside section. This suggests that:

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the leaching agents of nature.

3. By using the core for analysis, the effects of leaching are eliminated and consequently more weight may be attached to the age-determination.

4. The lower ratio of the outer layer is unusual, but this may be due to the fact that lead has been removed much faster than the thorium or uranium resulting in a lower ratio and consequently a lower age result. Alter and Yuill,[1] in analysing a single crystal of Wilber-force uraninite, also obtained a lower ratio in the outside layer of their crystal.

5. The variation of the thorium content in various sections of the crystal is of great interest. This variation is similar in direc-tion to that noticed by Alter and Yuill,[1] and Alter and Kipp.[2] This phenomenon exists in all previous cases where methods have been used to detect it. It would be of great interest to examine, in a like manner, crystals of uraninite from other localities.

6. The lead content of the middle section is a little higher than that of the core, and correspondingly the uranium and thorium con-tents are higher than those of the core. The fact that this is so, and that the ratios of the two inner sections are close, lends support to the accuracy of the constant "K" in the age formula, whereby the thorium is placed on a basis of equal lead-producing power as uranium.

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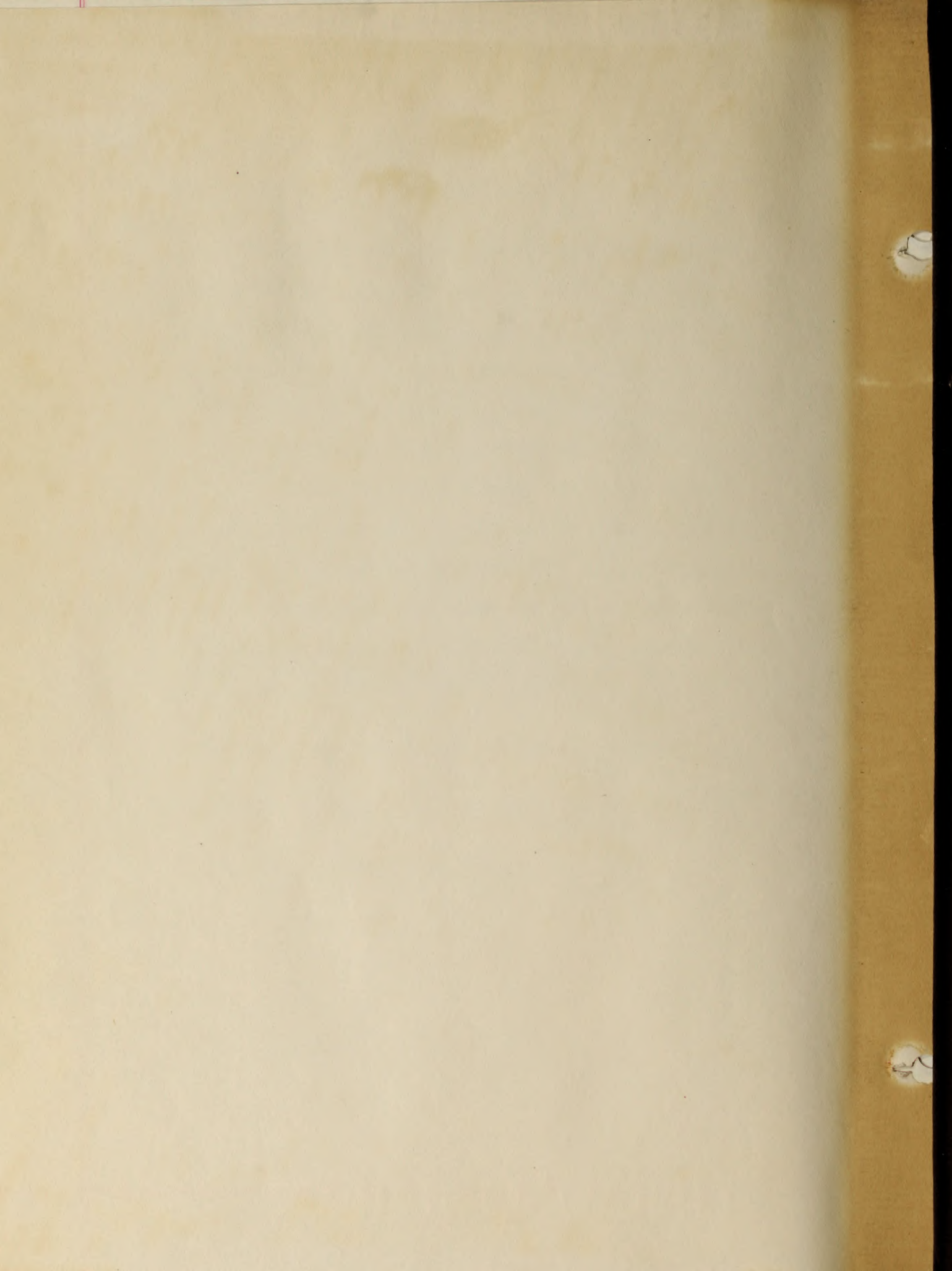
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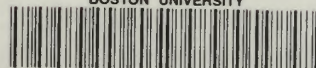14. Rutherford and Soddy: Trans. Chem. Soc., 81: 837-
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